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Donald A. Jaworske
Lewis Research Center
Cleveland, Ohio

and

Reza Zinolabedini
Cleveland State University
Cleveland, Ohio

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Donald A. Jaworske
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

and

Reza Zinolabedini
Cleveland State University
Cleveland, Ohio 44115

SUMMARY

The resistance of pitch-based graphite fibers was monitored, in situ, during a series of bromine intercalation experiments. The threshold pressure for the bromine intercalation of pitch-based fibers was estimated to be 102 torr. When the bromine atmosphere was removed from the reaction chamber, the resistivity of the intercalated graphite fibers increased consistently. This increase was attributed to loss of bromine from the perimeter of the fiber. The loss was confirmed by mapping the bromine concentration across the diameter of single intercalated fibers with either energy dispersive spectroscopy or scanning Auger microscopy. A statistical study comparing fibers intercalated in bromine vapor with fibers intercalated in bromine liquid showed that similar products were obtained with both methods of intercalation.

INTRODUCTION

Carbon fibers play an important role in the aerospace industry, particularly in the form of light weight, high strength composite structures (ref. 1). Their role should expand as improvements are made in carbon fiber technology. One area of research which shows considerable promise is graphite fiber intercalation. The electrical conductivity of graphite host fibers can be improved significantly by inserting the appropriate guest species between the carbon layers. Intercalating pitch-based fibers with bromine, for example, yields a graphite intercalation compound that not only has a conductivity comparable to stainless steel, but also exhibits long term stability over a wide range of environmental conditions (ref. 2).

This paper summarizes the results from several experiments designed to find the optimum conditions for the bromine intercalation of pitch-based graphite fibers. In each case, the progress of the intercalation reaction was monitored, in situ, with a four point probe. The parameter of interest, the partial pressure of bromine, was varied from 93 to 208 torr and the resulting changes in fiber resistance were recorded over time. In addition, the distribution of bromine across the diameter of several bromine intercalated fibers was studied. Finally the merits of intercalating with bromine vapor were compared to the merits of intercalating with bromine liquid.

METHODS

All measurements were obtained from Union Carbide pitch-based P-100 graphite fibers. The fibers were heat treated at 350 °C for several hours, in air, to remove the proprietary sizing. These fibers were chosen because of their commercial availability and their superior pristine characteristics (ref. 3). For example, the pristine resistivity of these fibers was 250 $\mu\text{ohm-cm}$.

For the in situ measurements, a single fiber was mounted on an oxidation-resistant, platinum-sputtered-alumina sample holder, which in turn, was placed in an all glass flow through reaction vessel. Platinum wires were used to connect the sample holder to a Keithley constant current source and a Keithley nanovoltmeter, in the conventional four point configuration. In all cases, the current through the fiber did not exceed 1 mA. The vapor pressure of the bromine in the reaction chamber was controlled by the temperature of the bromine reservoir, and the chamber holding the graphite was held at room temperature. Values for the vapor pressure of bromine were estimated from the temperature of the cooling bath, based on equation 1 (ref. 4):

$$\text{Log}_{10} P_{\text{Br}_2} = 5.82 - 638.25/(T (^{\circ}\text{C}) + 158.006) \quad (1)$$

The vapor transport method of intercalation was initiated by directing a small stream of nitrogen into the bromine chamber and the nitrogen-bromine mixture was then directed into the reaction chamber. After passing through the reaction chamber, the nitrogen-bromine mixture was directed into a gas scrubbing bottle for disposal. When the desired fiber resistance had been reached, the bromine vapor was flushed from the reaction chamber with pure nitrogen.

The fibers for the bromine distribution experiments were prepared, in bulk, by a similar vapor transport method. In this case, the fibers were placed in a static bromine atmosphere at room temperature. The reaction times were in excess of 24 hr, to ensure complete intercalation. After intercalation, the fibers were kept at ambient laboratory conditions until needed. Random samples were subjected to either energy dispersive spectroscopy (EDS) or scanning Auger microscopy (SAM). Standard instrumental operating procedures were used in both instances.

In the bromine vapor versus bromine liquid experiments, strands of P-100 graphite fiber were intercalated in either the vapor or the liquid, for a period exceeding 24 hr. To evaluate the relative effectiveness of each intercalation technique, several randomly chosen fibers were selected from each sample set, and their electrical resistivities were measured. Histograms of electrical resistivity values versus frequency of occurrence were developed for each sample set and the sets of data were compared statistically.

RESULTS AND DISCUSSION

The rate of intercalation, as measured by the four point method, depended on the vapor pressure of the bromine, providing the vapor pressure was above the critical threshold pressure (ref. 5). Resistance versus time curves for a "rapid" intercalation, a "slow" intercalation, and "no" intercalation (for

bromine vapor pressures of 208, 118, and 93 torr, respectively) are shown in figure 1. Experiments performed at intermediate vapor pressures showed no clear-cut trend between reaction rate and vapor pressure, suggesting that other experimental parameters such as the flow rate of bromine into the reaction chamber or variations in the fiber surface from fiber to fiber may be important in characterizing the rate of reaction.

One surprising feature exhibited by the data in figure 1 was the downward trend in resistance (illustrated by the 118 torr data) that occurred after the initial rapid decline in resistance had taken place. This downward trend was observed to various degrees in the other experiments performed at intermediate vapor pressures. Such a downward trend was not observed in similar ferric chloride experiments, where the resistance value reached a plateau (ref. 6). As a result of this downward trend, most of the bromine intercalated P-100 fibers eventually reached the same degree of intercalation (i.e., resistance ratio), as measured by the four point method. (The bromine data presented in fig. 2, showing the resistance ratios at the end of each experiment prior to bromine removal, illustrate the uniformity of the resistance ratio.)

Another surprising feature exhibited by the data in figure 1 was the increase in resistance that occurred as the bromine vapor was swept from the reaction vessel by nitrogen (as illustrated by the 208 torr data). This upward step in the resistance ratio was observed in every case, to varying degrees; and was tentatively attributed to loss of bromine from the perimeter of the fiber.

Shown in figure 2 are the final resistance ratios, obtained while the fiber was in equilibrium with either bromine or nitrogen, as a function of bromine vapor pressure during preparation. Also included in figure 2, for comparison, is the final resistance ratio (measured in situ) of a fiber intercalated in liquid bromine. The threshold pressure was estimated from this diagram to be about 102 torr. This value was somewhat larger than the value of 53 torr estimated by Hookey (ref. 5) for pyrolytic graphite cylinders with a similar number of exposed graphite layers. Both the bromine and the nitrogen data are presented in this figure to emphasize the uniform change in R/R_0 that occurs during the nitrogen purge step when the intercalation reaction goes to completion.

In subsequent experiments, the intercalation reaction was quenched prior to completion, via the nitrogen purge. The increases in resistance ratio during these purge steps were not uniform. Figure 3 summarizes the increases in resistance ratio upon nitrogen purge for a series of intercalations, ranging from partial intercalation to complete intercalation. The data in this figure do not describe a linear relationship, rather, the fibers apparently lose a greater fraction of their resistivity during the nitrogen purge step when they are not fully intercalated initially. According to figure 3, the loss in resistivity is greatest at an R/R_0 value (in bromine) of about 0.3.

To model this curvilinear behavior, the cross-sectional area of a hypothetical fiber (with a radius of 5.5 μm) was divided into three annular regions. The value of the resistivity for the inner region was varied from 0 to 250 $\mu\text{ohm-cm}$; the value of the resistivity for the outer region was either the same as the inner region, for a surrounding bromine atmosphere, or 250 $\mu\text{ohm-cm}$, for a surrounding nitrogen atmosphere; and the value of the

resistivity for the intermediate region was a weighted average of the values of the inner region and the outer region. The best fit of the experimental data (as shown by the solid line in figure 3) was obtained when the three annular regions were separated by interfacial radii of 2.5 and 3.5 μm . This model would suggest that when the fiber is in a bromine environment, the bromine is distributed evenly across the diameter of the fiber, but when the fiber is not in a bromine environment, the bromine is lost to a constant depth of about 2 μm , regardless of the degree of bromine intercalation.

To further confirm this hypothesis, the amount of bromine at several different locations across the diameter of a single bromine intercalated P-100 fiber was determined by energy dispersive spectroscopy (EDS). The bromine results, obtained at 11900 eV, are presented in figure 4. According to the EDS results, the loss of bromine is most noticeable in the outer 1-2 μm of the fiber. Based on the energy settings used during the experiment, the sampling depth for the EDS analysis was about 10 μm . On the other hand, the concentration of bromine near the surface of a bromine intercalated fiber was determined by depth profiling, using scanning Auger microscopy (SAM) (ref. 7). These results are shown in figure 5. According to the SAM results, no Br was detected at the surface, to a level of 3 nm, (see insert of fig. 5); and a very minor increase in Br concentration was noted through the top 40 nm of the surface. Since the end of the fiber is similar in morphology to the surface, the EDS results mentioned above may have underestimated the actual value of bromine across the diameter of the fiber, although the impact of these edge effects on the relative distribution of bromine should be minor. In either case, both techniques confirmed that the bromine concentration diminished in the outer skin of the fiber, probably after the fiber was removed from the bromine atmosphere. The loss of bromine, however, was not as severe as the model seemed to suggest.

The data point in figure 2 representing the in situ measurement during a liquid bromine intercalation experiment appears to be consistent with the other data gathered during the vapor bromine intercalation experiments. To compare vapor bromine intercalation with liquid bromine intercalation, three sets of bromine intercalated P-100 fibers were prepared, two in the vapor environment and one in the liquid environment. The fibers in the first vapor set were in bundles and the fibers in the second vapor set were separated. The three resistivity histograms, shown in figure 6, were compared statistically using the t-test (ref. 8).

Probability graph paper was used to check the resistivity distribution for each histogram. The plots indicated that the resistivity distributions for all three sample sets were normally distributed. The t-test was applied to the three sample sets to determine whether they came from the same resistivity population. The first calculated t value, obtained from the comparison of the first vapor sample set (bundled fibers) and the liquid sample set, showed that the population mean resistivities were significantly different. However, the second calculated t value, obtained from the comparison of the second vapor sample set (separated fibers) and the liquid sample set, showed that the population mean resistivities were from the same population with a confidence level of more than 85 percent.

The discrepancy between the bundled and the separated fibers may be due to insufficient time or bromine vapor pressure during the first bromine vapor intercalation process.

CONCLUSIONS

Above a threshold pressure of about 102 torr, the rate of bromine intercalation of single Union Carbide P-100 fibers varied from minutes to hours. However, given enough time, the final resistivity value consistently reached about 18 $\mu\text{ohm-cm}$, or 7 percent of the pristine resistivity value. Minutes after the bromine gas was swept from the reaction chamber, the resistance ratio increased, suggesting a partial loss of bromine from the fiber. This increase resulted in a resistivity value $\sim 45 \mu\text{ohm-cm}$, or 18 percent of the pristine resistivity value. The observed increase in resistance ratio was greater for fibers not fully intercalated initially. Mathematical modeling of the data seemed to suggest that bromine was lost from the outer 2 μm of the fiber when the fiber was removed from the bromine environment. EDS and SAM analysis confirmed such a bromine gradient in the skin of the fiber, but the observed loss of bromine was not as great as the model suggested. A statistical comparison of several bromine intercalated fiber populations showed that fibers intercalated in the vapor could achieve the same resistivity as fibers intercalated in liquid, to a t-test confidence level greater than 85 percent; providing adequate time and bromine vapor pressure were available.

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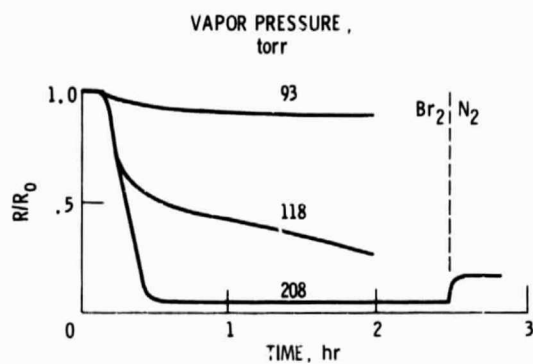


Figure 1. - Resistance ratio vs. time, at three different bromine vapor pressures.

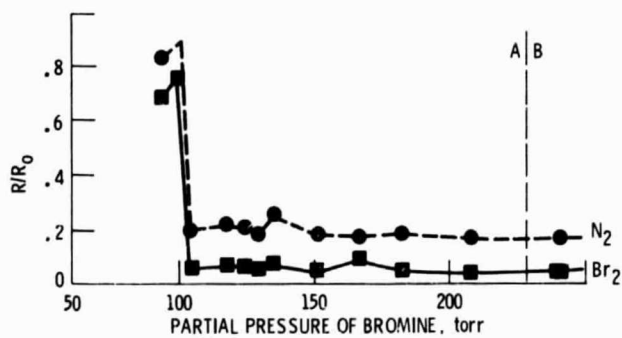


Figure 2. - Final resistance ratios vs. bromine vapor pressure during preparation, either in a nitrogen environment or in a bromine environment. Samples in region A were prepared in bromine vapor, those in region B were prepared in bromine liquid.

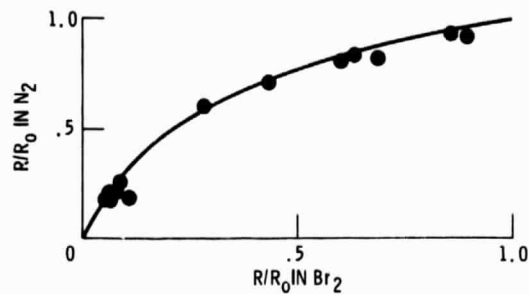


Figure 3. - Increases in fiber resistance ratio after the nitrogen purge.

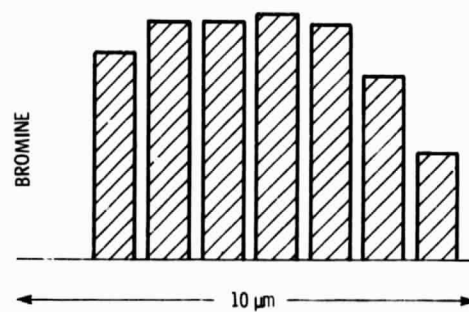


Figure 4. - Relative bromine concentration across the diameter of a single fiber, as measured by energy dispersive spectroscopy.

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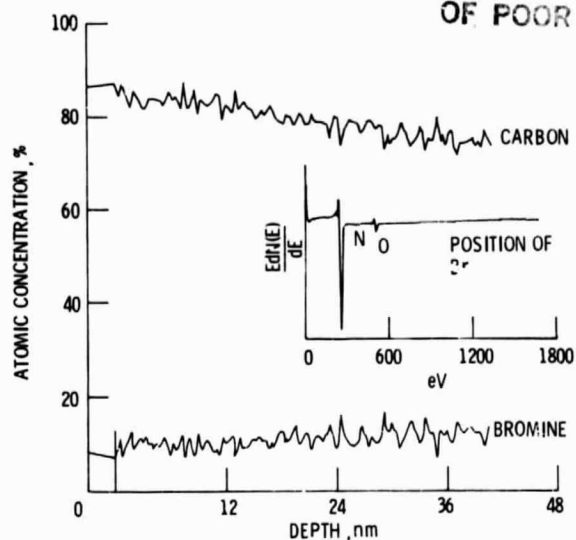


Figure 5. - Bromine concentration in the top 40 nm of a single fiber, as measured by scanning Auger microscopy. The inset shows the Auger spectrum obtained at the surface level, with the expected location of the bromine peak highlighted. Note, in the absence of bromine, the figure shows a base-line value for the atomic concentration of bromine of approximately 7 percent.

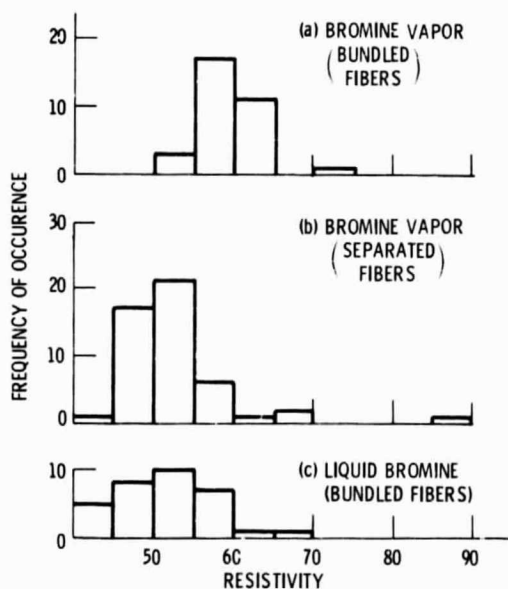


Figure 6. - Histograms of fiber resistivity, for three bromine intercalated fiber populations. Resistivity values for population 6b were obtained from J. R. Galer and D. Marino, NASA Lewis Research Center.

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